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# Chemical reactivity of solid [$Pt_nC_{60}$] towards carbon monoxide

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## Abstract

Evidence of chemical reactivity of solid platinum-fullerene [$Pt_nC_{60}$] compounds towards carbon monoxide is presented. The interaction was systematically studied by means of infrared spectroscopy, X-ray powder diffraction and thermogravimetric analysis. The interaction of carbon monoxide, even under low pressure, is confirmed by the appearance of infrared absorption bands in the CO stretching region at 2064, 2014 and 1991 $cm^{-1}$ for the carbonylation products. The exceptions were those products with low Pt:$C_{60}$ ratios, which also displayed bands at 1870 and 1830 $cm^{-1}$. The data suggest that the CO coordination depends on the specific morphology of the solids, the original Pt:$C_{60}$ ratio, and the carbon monoxide nominal pressure. Therefore, these results indicate the formation of [$(CO)_xPt]_m$ species supported in a fullerene matrix mixed with [$Pt_{n-m}C_{60}$] compounds. As there is a competition between carbon monoxide and fullerene molecules for the electronic density at the platinum centers, the nature of the CO interaction with [$Pt_nC_{60}$] was found to be destructive, leading to the displacement of the latter. Nevertheless, the platinum-carbonyl species formed presents relatively high stability, as shown by desorption tests.

*Keywords:* A. Fullerenes; A. Amorphous materials; C. Infrared spectroscopy; B. Chemical synthesis

## 1. Introduction

The diffusion of gaseous molecules into the interstitial cavities of solid fullerenes is well documented in the literature [1a–d]. Moreover, the adsorption of nitrogen and argon at 77 K on solid fullerenes has been reported to be less effective than in graphite [2]. Attempts to employ fullerenes as support of metallic particles in heterogeneous catalytic processes have not attracted much attention when compared to the most common supports, as for example amorphous carbon [3]. These results could be due to the low superficial area (ca. 5 $m^2/g$) and low sublimation temperature (ca. 700 K) of fullerenes [4]. Nevertheless, a combination of the properties of conventional supports, affording high superficial areas, such as silica and fullerenes, led to more fruitful applications in catalytic processes [3]. Therefore, structural and electronic properties of fullerenes can be investigated in order to obtain new and suitable materials for catalytic and gas sensor applications, mainly transition metal fullerene compounds [5a–c].

The coordination of fullerenes to electron rich transition metals such as palladium, platinum and ruthenium leads to loss of crystallinity, originating insoluble solids whose catalytic properties are similar or even superior to the metallic dispersions over amorphous activated carbons [6a–c]. In comparison to pure fullerene, those novel materials have each metal atom linked to two adjacent fullerene molecules without forming clusters, and superficial area ca. 20-fold higher, affording atomic dispersion properties [7a–c].

Herein we report chemical reactivity evidences for solid platinum-fullerene compounds towards carbon monoxide. The interaction was systematically studied by means of infrared spectroscopy, and the products were also analyzed by X-ray powder diffraction and thermogravimetric analysis (TGA). The absorptions in the CO stretching region in the infrared spectra show that under carbon monoxide pressure there occurs the formation of carbonyl species containing [$Pt_nC_{60}$]. Moreover, the carbon monoxide molecules coexist

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in different coordination sites in the carbonylated products prepared under high pressure, even after heating treatment under reduced pressure, suggesting a strengthening of the Pt–CO bond. The displacement of fullerene molecules from the platinum coordination sphere was also observed under high pressure conditions with a reduction in the formation of carbonyl species.

## 2. Experimental

Platinum-fullerene [$Pt_nC_{60}$] compounds were prepared as described elsewhere from the reaction between $Pt(cod)_2$ (cod = 1,5-cyclooctadiene) and $C_{60}$ [6b], and dried under reduced pressure at room temperature for removing all volatile species. Products with four different morphologies were obtained when the platinum to $C_{60}$ ratios varied in the range from 1 to 2 [7c], and were shown to be structurally similar, according to infrared absorption and Raman spectra, previously reported by us [6b]. Carbon monoxide (Air Liquide) and KBr (Aldrich) were grade products. The carbon monoxide chemisorption/desorption measurements over KBr pellets with about 5% [$Pt_nC_{60}$] were carried out by infrared absorption spectroscopy (Bomem MB, FT-IR). Samples were prepared by admitting carbon monoxide up to 1 bar into a Schlenk tube containing the samples. The high-pressure experiments were carried out in a stainless steel reactor fitted with Teflon. The same procedure, but in absence of KBr, was used for X-ray powder diffraction (Shimadzu XRD-6000, Cu Kα) and TGA analysis (Shimadzu TA-50) of the samples.

## 3. Results and discussion

The carbon monoxide chemisorption is commonly studied in solids by means of infrared spectroscopy, allowing the identification of the several ways of interaction. However, while the changes in the spectrum of the adsorbed species, compared to the free molecule, are readily assigned, bands originated from the interaction between the adsorbent and adsorbate are not at all assigned. Moreover, the infrared technique allows a distinction between chemisorption and physical adsorptions: whereas the absence of new bands in the spectrum after an interaction does not necessarily mean a physical adsorption, their observation can be unequivocally associated to a chemisorption [8]. As mentioned above, the infrared spectra of pristine [$Pt_nC_{60}$] have no absorption bands in the region between 2100 and 1750 $cm^{-1}$. Therefore, when a band is observed in this region after exposing the samples to carbon monoxide it will be characteristic of the latter. In Table 1 are listed the wavenumbers of the absorptions observed in the infrared spectra of the platinum-fullerene compounds subjected to 1 bar of carbon monoxide for 1 h. They clearly form two sets, which are related by the amount of platinum.

Table 1
Wavenumbers of infrared absorptions in the CO stretching region observed for [$Pt_nC_{60}$] exposed to 1 bar of carbon monoxide for 1 h

| $Pt:C_{60}$ ratio | $\nu_{CO}$ ($cm^{-1}$) | |
|---|---|---|
| | Terminal | Bridging |
| 1.0; 1.2 | 2064 (S), 2014 (s), 1991 (s) | 1871 (w), 1830 (w) |
| 1.5; 2.0 | 2066 (S), 2014 (w), 1990 (w) | – |

Intensities: S = strong; s = shouder; w = weak.

The observation of more than one CO stretching absorption band in the infrared spectrum may be ascribed to the existence of different chemisorption sites. Moreover, the simultaneous observation of typical absorption bands for terminal and bridging carbonyl species with different intensities suggests that the surface is heterogeneous to a large extent. It should be noted, however, that the bands assigned to bridging carbonyls are observed only in the spectra of the two compounds whose platinum content is close to one. On the other hand, the other two compounds with $Pt:C_{60}$ ratios greater than 1.5:1 do not show such carbonyl species. This behavior could be attributed to a facile saturation of platinum coordination sites in the first two compounds, which present less available coordination sites than their higher platinum content counterparts.

The thermal stability of the platinum-fullerene compounds was also investigated by a thermogravimetric study under synthetic air before and after CO chemisorption, in the temperature range between 25 and 600 °C. The results, listed in Table 2, suggest that the formation of carbonyl species implies less thermal stability for the two compounds whose $Pt:C_{60}$ ratio is close to one, presumably due to the displacement of fullerene from the platinum coordination with the possible formation of unstable platinum carbonyl species, which decompose more rapidly under the air flow when compared to the parent platinum-fullerene compounds. Such observation suggests that in these compounds fullerene exclusion from platinum coordination is more

Table 2
Decomposition temperatures of pristine [$Pt_nC_{60}$] and of their carbonylated products as measured by TGA analysis

| $Pt:C_{60}$ ratio | $T_{dec.}$ (K) | |
|---|---|---|
| | Pristine | CO exposed |
| 1.0 | 596 | 515 |
| 1.2 | 582 | 526 |
| 1.5 | 536 | 538 |
| 2.0 | 543 | 548 |

Defined as the temperature of maximum weight loss.

severe in comparison with their high platinum content analogues.

Analysis of the solid residues after heating at 600 °C of all four compounds by X-ray powder diffraction showed that only metallic platinum was formed. It is worth of mention that the conditions employed in the TGA experiments (air flow 10 ml/min, heating rate 5 °C/min) afford data that are unable to ascribe to different contents of CO, and that fullerene solids deposited onto cool parts of the thermobalance were not detected.

Complementary studies were carried out to investigate the stability and the reversibility of the interactions of these novel platinum-fullerene compounds with carbon monoxide. Although the compounds have been maintained under reduced pressure for 15 h, no noticeable change was observed in the infrared spectra. This result also confirms the carbon monoxide chemisorption over $[Pt_nC_{60}]$, with the formation of relatively stable carbonyl species, instead of a mere physical adsorption. Nevertheless, the products were heated at 373 K under vacuum for about 5 h in another experiment with the loss of bridging carbonyls and an absorption band shift of the remaining terminal carbonyl from 2064 to 2059 $cm^{-1}$. The small shift of the latter band when compared to the non-treated sample can be attributed to a decrease in the concentration of chemisorbed terminal CO molecules, in terms of a lower dipolar interaction among chemisorbed adjacent CO molecules. The reversibility of the CO chemisorption was also tested by submitting the heated pellets to 1 bar of carbon monoxide pressure for 1 h, but only the 2059 $cm^{-1}$ band was observed without significant changes in intensity.

It is interesting to note that similar results were reported in the literature, particularly in investigations on oxide-supported platinum [9]. Moreover, it was also observed that the nature of the support has strong influence on the stretching frequency of metallic carbonyls. Generally, the higher the acidity of the support, the higher the stretching frequencies of the chemisorbed carbon monoxide [10]. This effect is commonly explained by the electronic density donation from the metal to the support. In terms of HOMO and LUMO frontier orbitals in the MO approach, the electronic states of the surfaces near the Fermi level in solid materials are equivalent to the HOMO. The synergistic effects of CO chemisorption manifest themselves in a lowering of the CO bonding stretching frequency, due to the favoring of the $\pi$ back-donation from the filled metal d orbitals to the empty $2\pi^*$ molecular orbitals of carbon monoxide.

Concerning the influence of the nature of the support in the stretching frequency of the CO vibration, fullerenes behave like an electron deficient polyolefin with $\pi$-acid characteristics [11]. Therefore, some competition is expected between $C_{60}$ and CO for the electronic density at the platinum atom, as was indeed suggested by the strong shift in the CO stretching frequency from the free CO and the chemisorbed species. In order to investigate the role of the fullerene molecule, until here treated as a mere support, a further experiment was carried out. The infrared spectra of the samples exposed to CO were measured in the range from 2500 to 400 $cm^{-1}$. It was noted after CO exposure that the spectra of the platinum-fullerene compounds displayed in addition to the usual strong carbonyl bands a weak absorption at 476 $cm^{-1}$ assigned to a Pt–CO vibration mode [12]. Other four sharp and intense absorption bands, observed at 526, 577, 1182 and 1428 $cm^{-1}$, are characteristic of the uncoordinated fullerene molecule. All these new bands are superimposed on the spectra of the platinum-fullerene compounds, suggesting that the fullerene molecules were partially displaced from the platinum coordination. The spectra of the platinum-fullerene compounds and of the carbonylated products are shown in Fig. 1.

It should be mentioned that the same behavior was observed in the presence of solvent. When a suspension of $[Pt_nC_{60}]$ in toluene is treated with a gentle carbon monoxide stream, a magenta solution is formed in a few minutes. After solvent removal under vacuum at low temperature, a brownish solid is recovered. The infrared spectra of this solid either in KBr pellet or in $CH_2Cl_2$ solution show absorption bands in the CO stretching region, at 2058, 2016 and 1978 $cm^{-1}$. However, the solid decomposes rapidly under normal conditions, and the infrared absorption bands are no longer observed.

As mentioned earlier, platinum-fullerene compounds under ordinary CO pressures behave distinctively with the platinum content. In order to verify this behavior, high-pressure experiments were performed by submitting the compounds to carbon monoxide pressures from 3 to 25 bar. Whereas a nominal pressure of 3 bar increased only the intensities of the absorption bands, the pressure of 25 bar induced new bands at 2013 and 1989 $cm^{-1}$ in the infrared spectra. A substantial increase in the intensity of the whole spectrum was also noted, as shown in Fig. 2.

The absorption bands related to the infrared spectrum of pure $C_{60}$ shown in Fig. 2 have their intensities enhanced with an increase in the carbon monoxide pressure, suggesting that the pressure promotes the removal of fullerene molecules from the platinum coordination. One can argue that under these conditions there is formation of $[(CO)_xPt]_m$ species mixed with $[Pt_{n-m}C_{60}]$ compounds, where $n$ is the original platinum fullerene ratio, $m$ is the amount of platinum excluded from fullerene coordination and $x$ denotes the nuclearity of the carbonyl species.

Concerning the stability of the carbonyl species formed under high-pressure conditions, a desorption test was conducted by maintaining the samples overnight under vacuum. Since no noticeable change was observed in the infrared spectra, the result reinforced the previous conclusion about a relative high stability for the carbonyl species. However, there was a shift of the band assigned to the terminal carbonyl species formed at a pressure of 25 bar from 2064 to 2052 $cm^{-1}$, and the absence of the bands at

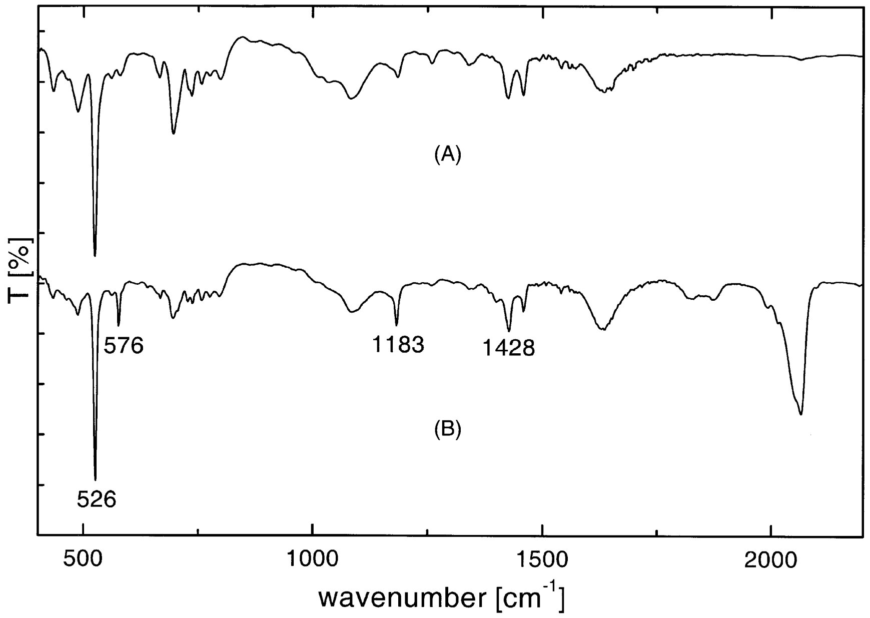

Fig. 1. Transmitance IR spectra of pristine [Pt$_n$C$_{60}$] (A) and after exposition to CO at 1 bar (B). The fullerene absorptions are marked.

2013, 1989, 1879 and 476 cm$^{-1}$ for the samples heated to 373 K for 1 h in vacuum, as shown in Fig. 3.

It is interesting to note that the X-ray powder diffractograms of the solids exposed to CO show distinctive profiles with respect to the platinum content. The solids with lowest platinum content display broad and weak peaks assigned to the formation of metallic platinum (prominent peak near corresponding to the Pt [111] diffraction) and presumably of crystalline fullerene (peak near $2\theta = 30$, corresponding to the fcc C$_{60}$ [311] diffraction). On the other hand, the two solids of higher platinum content exposed to carbon monoxide did not present distinct peaks in the region between $10 \leq 2\theta \leq 50$. Despite the high noise levels of these diffractograms, such distinctive profiles further support our initial assumption of different degrees of saturation upon low pressures of carbon monoxide.

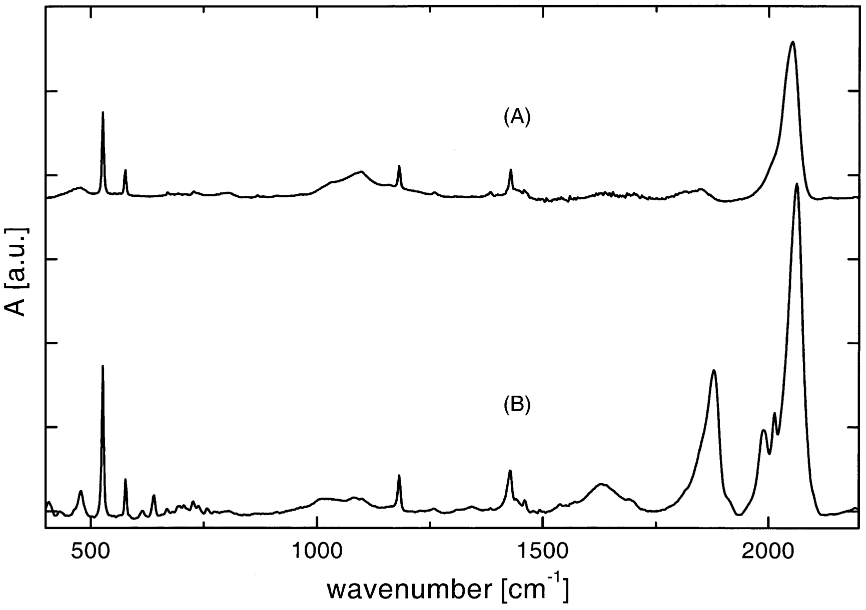

Fig. 2. Absorbance IR spectra of [Pt$_n$C$_{60}$] submitted to CO at 3 bar (A) and at 25 bar (B).

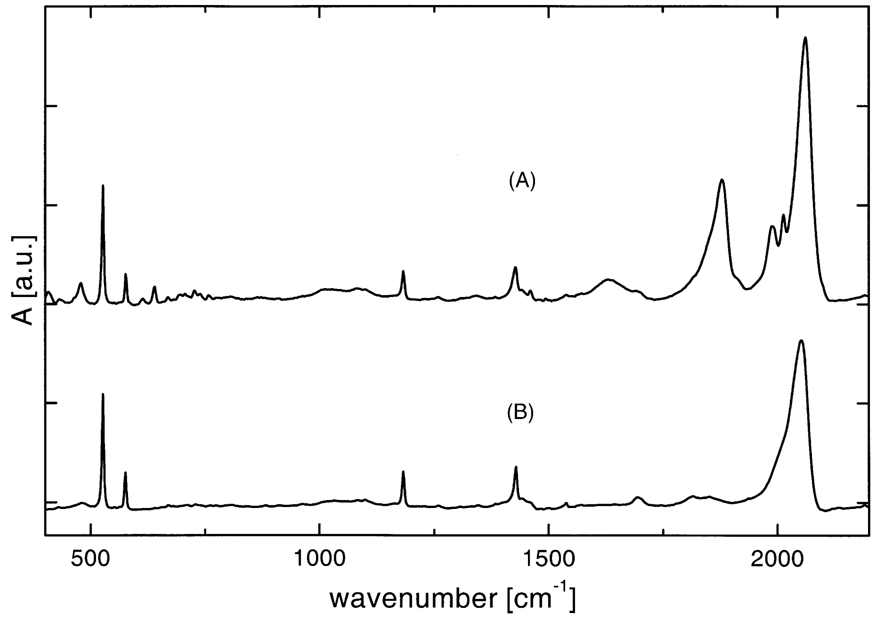

Fig. 3. Absorbance IR spectra of [$Pt_nC_{60}$] submitted to CO pressure of 25 bar (A) and after heating at 373 K under vacuum for 1 h (B).

## 4. Conclusion

Infrared spectroscopy, TGA and X-ray powder diffraction suggest the formation of $\{(CO)_xPt_{n-m}C_{60}\}$ species due to chemical interaction between CO and [$Pt_nC_{60}$]. These platinum-carbonyl species supported in a fullerene matrix are mixed with [$Pt_{n-m}C_{60}$] compounds, where the value of $(n-m)$ depends on several aspects of the original Pt:$C_{60}$ ratio and the carbon monoxide nominal pressure. The results also point to a distinctive behavior upon CO coordination, which depends on the specific morphology of the solids. The nature of the CO interaction over [$Pt_nC_{60}$] is found to be destructive, that is, the competition between carbon monoxide and fullerene molecules for the electronic density at the platinum atoms leads to a displacement of the latter. Nevertheless, it is was also shown that the fullerene molecules do not behave as an inert support, judging from the shifts observed in the stretching frequencies of the chemisorbed CO vibration when compared to the free molecule. Further, in comparison with other mixed platinum olefin carbonyl compounds the interaction of the newly formed platinum-carbonyls with the fullerenes is noticeable [13]. Indeed, the formation of relatively stable carbonyls in the system suggests some stabilizing role for the fullerene 'support'. It should be anticipated that the platinum-fullerene compounds present an interesting system for further studies concerning the sensitivity towards specific gaseous species, or even as precursors in fullerene organometallic chemistry.

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